Gas-Chromatographic Detection of Phthalic Acid Esters

by Eugene F. Corcoran*

Each second, the rivers of the world add 10^9 kg of fresh water to the oceans, and with this water comes tremendous quantities of salts, clay minerals, and other suspended solids. Although the Amazon River makes the largest contribution of fresh water to the sea, its waters are relatively uncontaminated. On the other hand, the Mississippi River, the third largest river, which delivers only about one-twelfth the volume of the Amazon River, flows many hundreds of miles through rich, extensively cultivated farm land and some of the most highly industrialized areas in the world. Thus, in addition to the salts and suspended material normally present in river water, the waters of the Mississippi could conceivably carry agricultural and industrial wastes from land drainage into the Gulf of Mexico.

The surface waters and stream bed materials of the Mississippi River and other rivers of the United States have been monitored for a number of years through the coordinated efforts of federal, state, local and private agencies. Green et al *(1)* summarized the results of these studies on surface waters for the years 1958–1966, while Barthel et al. *(2)* did much the same for stream-bed material. However, the monitoring program does not follow the river water nor stream bed material out into the Gulf of Mexico. A program of study designed to measure the concentration of trace metals and chlorinated hydrocarbon pesticides in the effluents of the Mississippi River and estuaries of the northeast Gulf of Mexico was begun in 1970. Some of the results of this program will be discussed in this report.

During April and May 1970 samples of water, suspended material, sediments and benthic organisms from the Mississippi River, the Mississippi River delta system and the adjacent Gulf of Mexico were collected for chlorinated hydrocarbon pesticide analyses *(3)*. A total of 41 stations were occupied during this cruise. In September 1971, a 65-station cruise collected similar samples from the area off Escambia and Perdido Bays. The water samples were collected in large Niskin samplers. On the 1970 cruise the samples were filtered immediately through Whatman GF/C glass filters and extracted with hexane immediately, while on the 1971 cruise the water samples were placed in glass bottles and extracted with hexane at the laboratory. In each case the hexane extract was brought to a 5-ml volume with Kuderna-Danish concentrator. The determinations were made on a Beckman GC-5 gas chromatograph equipped with a helium arc emission electron capture detector. Because of their ability to separate, closely related chlorinated hydrocarbons, especially that of *p,p'*-DDE and dieldrin, two chromatographic column systems were used: 5% QF-1 on 80/90 Gas Chrom Q, and 1.5% OV-17, 1.95% QF-1 on 80/90 Gas Chrom Q. Figure 1 shows a chromatogram of a hexane

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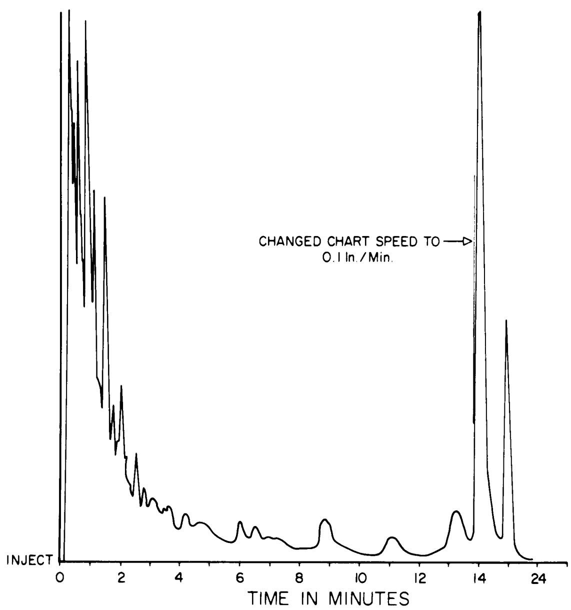

FIGURE 1. Chromatogram of hexane extract of surface water collected in the Gulf of Mexico near South Pass off the Mississippi River. Peaks with elution times less than 13 minutes are chlorinated hydrocarbon residues. Peaks with elution time greater than 13 min. are phthalic acid esters. Conditions: column, 1/8 in. x 6 ft stainless steel packed with 1.5% OV-17/1.95% QF-1 on 80/90 mesh Gas Chrom Q; chromatograph, Beckman GC-5 with EC detector; oven temperature, 200°C; detector temperature, 250°C; helium flow, 25 ml/min.

extract of the surface waters collected near South Pass off the Mississippi River delta. No additional clean-up has been made on this hexane extract. The hexane was simply dried over anhydrous sodium sulfate, concentrated to 5 ml, and a 5 μl shot was injected into the gas chromatograph.

As can be seen from this chromatogram, a whole spectrum of chlorinated hydrocarbon pesticides are represented. This spectrum includes residues of α-, β-, and δ-BHC, lindane, heptachlor, heptachlor epoxide, aldrin, dieldrin, and both p,p'-DDT, and o,p'-DDT and their derivatives.

However, the last three peaks on the chromatogram cannot be accounted for by pesticide residues. Since the chart speed has been changed from 0.5 in./min to 0.1 in./min, the peaks represent a relatively large quantity of material.

Because the elution time for this material added at least another 10 min to each sample analysis, our laboratory immediately launched an investigation into its identification and source. The possibility that this material was being introduced in the system of sampling or sample preparation was eliminated through a thorough investigation. This material was in the water samples and, to a lesser degree, was to be found in the particulates and sediments.

The behavior of these unknown substances was similar to that of the chlorinated hydrocarbon pesticides on Florisil columns, thus making it impossible to isolate them in this manner. The possibility that the material might be a PCB plasticizer was eliminated by securing Aroclor standards and making comparative chromatograms. TLC work indicated that this material was not chlorinated, as shown by subsequent treatment with silver nitrate solution, although when chromatographed on a silica gel column the material eluted as an aromatic.

One by one, the substituted phosphates, the carbamates, and sulfur were eliminated as possibilities. Finally, an extract of Tygon tubing was found to give similar chromatographic peaks. A literature search revealed that Jaeger and Rubin (*4*) had found two phthalic acid esters to be extracted from plastic tubing and plastic bags. Plasticizer samples were obtained from these authors and from Union Carbide. The two plasticizers that gave chromatographic peaks matching those found in the environmental samples were butylglycol butyl phthalate and di-2-ethylhexyl phthalate (DOP). Thus far, no further attempt has been made to confirm these identifications, nor has the concentration of these substances in each sample been calculated, but if the substance in this water sample from off the Mississippi River is assumed to be entirely di-2-ethylhexyl phthalate, its concentration is about 0.6 ppm. Moreover, if the effluent of the Mississippi River contained just one-third this concentration an amount equivalent to the yearly production (350 million pounds)

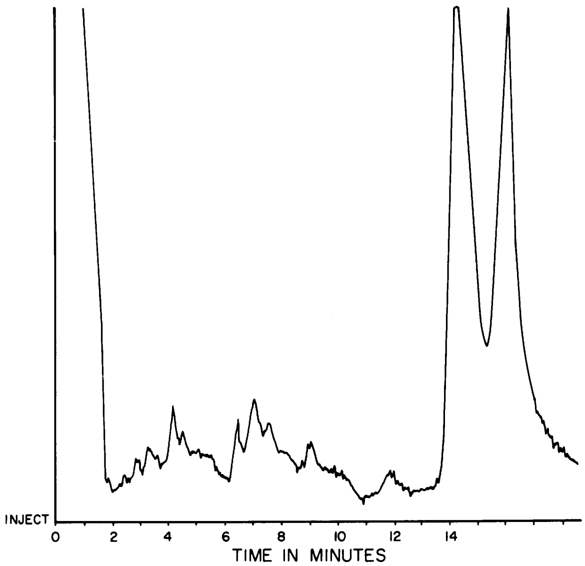

FIGURE 2. - Chromatogram of hexane extract of surface water collected in the northeast Gulf of Mexico (30°21'N, 86°48'W) showing two large phthalic acid ester peaks. Conditions: column, 1/8 in. x 6 ft stainless steel packed with 1.5% OV-17/1.95% QF-1 on 80/90 Gas Chrom Q; chromatograph, Beckman GC-5 with EC detector; Oven temperature, 200°C; detector temperature, 250°C; helium flow, 25 ml/min.

of this compound (*5*) would enter the Gulf of Mexico annually.

The waters off Escambia Bay (near Pensacola, Florida) also contain lesser amounts of these substances (Fig. 2), and even a lesser concentration has been found just recently in the clear blue waters of the Gulf Stream (Fig. 3). Briefly, phthalate acid esters can be detected by gas chromatography by using an electron capture detector. Like DDT and PCB, these esters seem to be attaining a widespread distribution in fresh waters of the Mississippi River and the marine coastal waters of the Gulf of Mexico and the Gulf Stream.

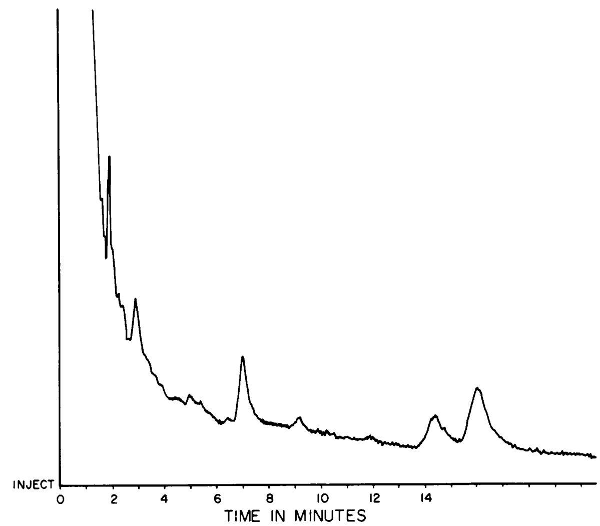

FIGURE 3. - Chromatogram of hexane extract of Gulf Stream surface water collected east of Miami, Florida showing lindane, aldrin, dieldrin residues and two small phthalic acid ester peaks. Conditions: column, 1/4 in. x 6 ft glass packed with 1.5% OV-17/1.95% QF-1 on 80/90 Gas Chrom Q; chromatograph, Beckman GC-5 with EC detector; Oven temperature, 200°C; detector temperature, 250°C; helium flow, 50 ml/min.

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